

AE

453



(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 0 760 531 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
05.03.1997 Bulletin 1997/10(51) Int. Cl.⁶: H01M 8/06, H01M 8/12

(21) Application number: 95113511.0

(22) Date of filing: 29.08.1995

(84) Designated Contracting States:
BE CH DE FR GB IT LI NL SE

(72) Inventors:

- Rostrup-Nielsen, Jens
DK-2830 Virum (DK)
- Christiansen, Lars J.
DK-3520 Farum (DK)
- Aasberg-Petersen, Kim
DK-2830 Virum (DK)

(30) Priority: 29.08.1995 DK 1129/94

(71) Applicant: Haldor Topsoe A/S
DK-2800 Lyngby (DK)

(54) Process for the production of electrical energy in an internal reforming high temperature fuel cell

(57) In a process for producing electrical energy in an internal reforming high temperature fuel cell, comprising steam reforming of a carbonaceous feed gas in the presence of a steam reforming catalyst in heat conducting relationship with electrochemical reactions in the fuel cell; and

electrochemically reacting the steam reformed feed gas in an anode compartment of the fuel cell, the improvement consists in adding a gaseous sulphur containing compound to the carbonaceous feed gas in an amount sufficient to obtain a sulphur coverage (θ) on the steam reforming catalyst of between 0.1 to 0.9.

EP 0 760 531 A1

EP 0 760 531 A1

Description

This invention is directed to a method of producing electrical energy in a high temperature fuel cell, and more particular, to improvements in the electrochemical conversion of chemical energy contained in a carbonaceous feed gas into electrical energy in high temperature fuel cells.

High temperature fuel cells like the solid oxide fuel cell comprise an electrolyte sandwiched between a cathode and an anode. Oxygen reacts with electrons at the cathode to oxygen ions, which are conducted through the ion-conducting ceramic electrolyte to the anode according to the reaction:

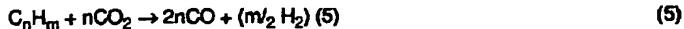
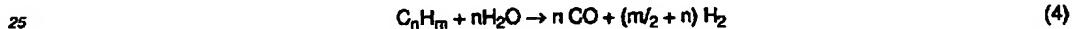


At the anode, oxygen ions combine with hydrogen and carbon monoxide to water and carbon dioxide thereby liberating electrons according to the exothermic reactions:



The above electrochemical reactions are in conventionally designed solid oxide fuel cells usually performed at temperatures of between 800°C and 1000°C.

The high operating temperatures employed in solid oxide fuel cells permit internal reforming of carbonaceous feed gas to anode fuel gas. The feed gas is, thereby, combined with steam and/or carbon dioxide and reformed within the fuel cell by the following endothermic reactions:



The reforming reactions (4) and (5) may be carried out directly on the anode, which in the known solid oxide fuel cells are usually made of metallic nickel or ruthenium supported on yttria-stabilized zirconia.

In order to enhance reforming of the feed gas, the gas is contacted with a specific steam reforming catalyst including nickel and/or ruthenium, supported on refractory carrier materials arranged internally within the cell in heat conducting relationship with the electrochemical reactions in the cell. Thereby necessary heat for the above endothermic reforming reactions is supplied by excess heat from the exothermic electrochemical reactions (2) and (3).

As an advantage of such a fuel cell, the need for external heat exchange is reduced or eliminated and the efficiency of the cell and the fuel cell plant increased.

Internal reforming of carbonaceous feed within a solid oxide fuel cell is, however, problematic. As known in the art, the steam reforming reactions proceed at a very high rate at the inlet portion of the catalyst or anode resulting in strong cooling at the cell inlet or formation of cold spots in the cell.

This is detrimental for the cell performance in several ways. A decrease in the cell temperature rapidly increases the ohmic resistance of the solid cell electrolyte, leading to reduced operating cell voltage of the cell. In addition, material problems related to thermal stress arising from differential temperatures of cell components at local cold spots and high temperature gradients in regions of the inlet portion of the cell reduce the cell lifetime.

A further problem, which usually occurs during steam reforming at very high temperatures as in the solid oxide fuel cell, is cracking of hydrocarbons, which leads to severe carbon deposition on the reforming catalyst or cell anode.

We have now observed that carbonaceous feed gas is reformed internally within a solid oxide fuel cell without the above problems, if the activity for reactions (4) and (5) of the steam reforming catalyst or the cell anode is reduced by partial poisoning the catalytic material with sulphur.

Based on this observation, the invention provides an improved method of producing electrical energy in an internal reforming solid oxide fuel cell comprising catalytic steam reforming carbonaceous feed gas internal and in heat conducting relationship with electrochemical reactions in the fuel cell; and

electrochemically reacting the steam reformed feed gas in an anode compartment of the fuel cell, the improvement of which consists in adding controlled amounts of a gaseous sulphur containing compound to the carbonaceous feed gas to obtain on surfaces of the cell, which are catalytic active in the steam reforming of the feed gas, a sulphur coverage of between 0.1 and 0.9 sulphur atoms per catalytic surface atom.

Through partial sulphur poisoning of the steam reforming catalytic active surface, the endothermic reforming reactions proceed at a lower rate, in particular, at the inlet portion of the cell having a high sulphur coverage, which results in a lower temperature drop in this region and a desirable smooth temperature profile in the cell.

Furthermore, the sulphur compound in the feed gas blocks partially the catalytic surface, which means that

EP 0 760 531 A1

adsorbed carbon atoms formed at high temperatures by cracking of hydrocarbons in the feed gas cannot be dissolved into the catalytic surface, which eliminates carbon formation on the surface.

5 Data from the literature (J. Catal. 85, 31, 1984) show that at high temperatures the reforming activity of nickel, which is the usual catalytic active ingredient of the catalytic surface in the cell, decreases at a sulphur coverage of between 0.2 and 0.5 by the power of about 3, whereas the rate of carbon formation decreases by the power of about 6.

It has further been observed that the presence of sulphur in an amount of up to 69 ppm H₂S in a pure hydrogen fuel gas has no significant impact on the electrode activity of the cell (B.G. Ong, D.M. Mason, Fuel Cell Seminar, Tucson, U.S.A., 1986).

10 It is, thus, possible to control the reforming rate internally of a solid oxide fuel cell, by adding small amounts of sulphur compounds to the feed gas, whereby excessive cooling of the cell in the inlet part due to high reforming rates is avoided.

The catalytic surface may comprise any of the metals known to be active in the steam reforming of hydrocarbons and to have affinity to sulphur. Preferred metals are nickel, ruthenium, gold, platinum or mixtures thereof, which are the usual catalytic active ingredients of the anode in a solid oxide fuel cell or of steam reforming catalysts.

15 As mentioned above, an advantage of the solid oxide fuel cell is the possibility to perform the steam reforming reactions directly on the anode without a specific reforming catalyst in the cell.

When using controlled amounts of sulphur compounds in the feed gas, the reforming rate on the internal reforming anode will be most reduced at the inlet of the anode, because of a low partial pressure of hydrogen in this region. As sulphur compound can be used H₂S or any compound that is converted to H₂S in the hydrogen containing fuel gas.

20 The above features and advantages of the invention will further be illustrated by means of computation models, showing the sulphur coverage profile on the nickel containing anode of a solid oxide fuel cell at different contents of sulphur in the feed gas together with the rate of the steam reforming reactions thereby obtained.

Example

25 In a first calculated experiment, the relative steam reforming reaction rate on a nickel surface in a conventional fixed bed containing nickel catalyst was calculated at different sulphur coverage rate on the nickel surface.

Sulphur coverage (θ_s) was determined by simulated hydrogen sulphide addition to a hydrocarbon containing feed gas to obtain a

$$30 \quad \theta_s = 1.45 - 9.53 \cdot 10^{-5} T(\text{°K}) + 4.17 \cdot 10^{-5} T(\text{°K}) \cdot \ln \frac{P_{H_2S}}{P_{H_2}}$$

35 between 0 and 50 ppm.

By use of the known formula

$$40 \quad \theta_s = 1.45 - 9.53 \cdot 10^{-5} T(\text{°K}) + 4.17 \cdot 10^{-5} T(\text{°K}) \cdot \ln \frac{P_{H_2S}}{P_{H_2}}$$

the sulphur coverage on the nickel surface was calculated as summarized in Table 1 below. The relative steam reforming rate (r) in the hydrocarbon feed gas at different sulphur coverages was calculated at an inlet temperature T of 1273°K by use of the formula

$$45 \quad r = r_o (1 - \theta_s)^3$$

wherein r_o is the steam reforming reaction rate at a zero sulphur concentration in the feed gas.

46 The relative steam reforming reaction rate at sulphur concentration of between 0 and 50 ppm H₂S/H₂ are summarized in Table 1.

EP 0 760 531 A1

Table 1

P_{H_2S}/P_{H_2} (ppm)	θ_s	r/r_s
0	0	1.000
0.1	0.4731	0.1462
0.5	0.5585	0.0861
1	0.5983	0.0667
2	0.6321	0.0498
3	0.6536	0.0416
5	0.6807	0.0326
10	0.7175	0.0225
50	0.8030	0.0076

As apparent from Table 1, small amounts of sulphur, which have, as mentioned before no adverse effect on the electrochemical reactions in the fuel cell anode chamber, caused a considerable decrease of the steam reforming activity.

In a second experiment the temperature profile within an internal reforming solid oxide fuel cell was calculated on an inlet fuel gas having a composition of

12 vol% H_2
28 vol% CH_4
4 vol% CO_2
56 vol% H_2O

The temperature profile calculated at a relative axial distance from 0 to 1 within an internal reforming chamber of a solid oxide fuel cell without addition of H_2S (□) and with addition of 3 ppm H_2S (○) to the fuel gas is shown in Fig. 1 of the drawing.

As seen from Fig. 1, the cell temperature drops abruptly from an inlet temperature of 1000°C to about 700°C in the inlet region after introduction of the sulphur free fuel gas and then inclines smoothly to 1000°C towards the anode outlet region.

When introducing the sulphur-containing fuel gas, only a slight temperature decrease from an inlet temperature of 1000°C to a minimum temperature of approx. 950°C is calculated for the sulphur containing fuel gas due to a decreased reforming activity of the catalytic surface.

Claims

1. In a process for producing electrical energy in an internal reforming high temperature fuel cell, comprising steam reforming of a carbonaceous feed gas in the presence of a steam reforming catalyst in heat conducting relationship with electrochemical reactions in the fuel cell; and
electrochemically reacting the steam reformed feed gas in an anode compartment of the fuel cell, the improvement consists in adding a gaseous sulphur containing compound to the carbonaceous feed gas in an amount sufficient to obtain a sulphur coverage (θ) on the steam reforming catalyst of between 0.1 to 0.9.

EP 0 760 531 A1

2. The process of claim 1, wherein the high temperature fuel cell is a solid oxide fuel cell.
3. The process of claim 1, wherein the steam reforming catalyst is arranged in indirect heat contact with the electro-chemical reactions in the anode compartment of the fuel cell.
5. The process of claim 1, wherein the steam reforming catalyst is arranged directly in the anode compartment of the fuel cell.
10. The process of claim 1, wherein the steam reforming catalyst comprises nickel as its active catalytic ingredient.

15

20

25

30

35

40

45

50

55

EP 0 760 531 A1

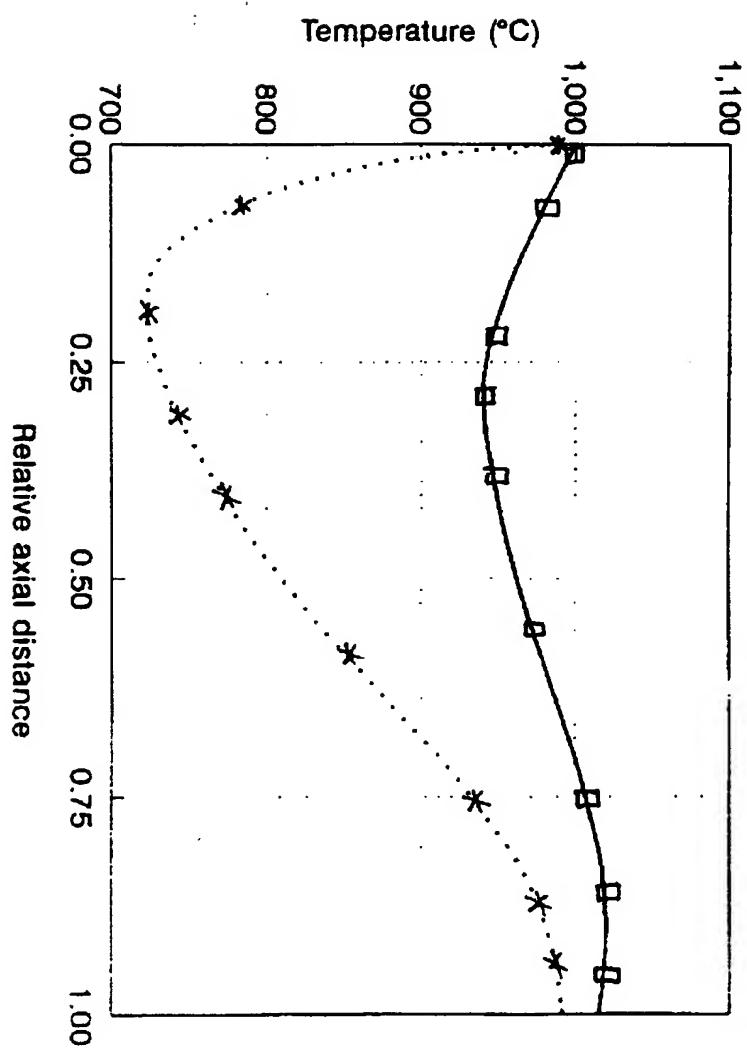


FIG. 1

EP 0 760 531 A1

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 11 3511

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.)		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim			
X	INTELEC'91 NOVEMBER 5-8 1991 KYOTO, JAPAN, pages 387-392, S. KANEKO ET AL 'RESERACH AND DEVELOPMENT ON TUBULAR TYPE SOLID OXIDE FUEL CELL' * page 390, left column, line 6 - line 9 * ---	1,2,4,5	H01M8/06 H01M8/12		
X	PROCEEDINGS OF THE 25TH INTERSOCIETY ENERGY CONVERSION ENGINEERING CONFERENCE AUGUST 12-17 1990 RENO, NEVADA, vol. 3, pages 201-206, T. TANKA ET AL 'DEVELOPMENT OF INTERNAL REFORMING MOLTEN CARBONATE FUEL CELL TECHNOLOGY' * table 2 *	1,3,5			
A	FIRST EUROPEAN SOLID OXIDE FUEL CELL FORUM PROCEEDINGS LUCERNE SWITZERLAND 3-7 OCTOBER 1994, vol. 1, 1994 pages 111-128, AASBERG-PETERSEN K 'Balance-of-Plant of SOFC Units for High Efficiency' * page 115 * * page 120, paragraph 1 * * page 125, last paragraph - page 126, paragraph 2 * ---	1,2,5	TECHNICAL FIELDS SEARCHED (Int.Cl.) H01M		
A	EP-A-0 076 019 (WESTINGHOUSE ELECTRIC CORP) 6 April 1983 * claims 1,3,5 *	1,2,4,5			
A	PATENT ABSTRACTS OF JAPAN vol. 018 no. 263 (E-1550) ,19 May 1994 & JP-A-06 044999 (MITSUBISHI ELECTRIC CORP) 18 February 1994, * abstract *	1,3			
--- -/-					
The present search report has been drawn up for all claims					
Place of search	Date of completion of the search	Examiner			
THE HAGUE	22 January 1996	D'hondt, J.			
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : informative document					
T : theory or principle underlying the invention E : earlier patent document, not published as, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document					

EP 0 760 531 A1

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 11 3511

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CI)
A	<p>CHEMICAL ABSTRACTS, vol. 109, no. 2, 11 July 1988 Columbus, Ohio, US; abstract no. 9330j, LEE A. L. ET AL 'Internal reforming development of solid oxide fuel cells: final report' * abstract * & REPORT 1987 DOE/MC/22045-2364, ---</p>	1,2,4,5	
A	<p>EP-A-0 414 573 (TONEN CORP ;PETROLEUM ENERGY CENTER FOUNDA (JP)) 27 February 1991 * page 5, line 2 - line 25; claims 1,6 * ---</p>	1,4	
A	<p>EP-A-0 173 904 (ENERGY RES CORP) 12 March 1986 * page 20, line 31 - page 21, line 27; claims 1,3,4,9,10; figure 5 * ---</p>	1,3,5	
A	<p>EP-A-0 497 332 (ENERGY RES CORP) 5 August 1992 * column 6, line 18 - line 35; figure 2 * ---</p>	1,3,5	
A	<p>PATENT ABSTRACTS OF JAPAN vol. 013 no. 150 (E-742) ,12 April 1989 & JP-A-63 310574 (TOKYO GAS CO LTD;OTHERS: 03) 19 December 1988, * abstract * -----</p>		TECHNICAL FIELDS SEARCHED (Int.CI)
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	22 January 1996	D'hondt, J	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons R : member of the same patent family, corresponding document			